

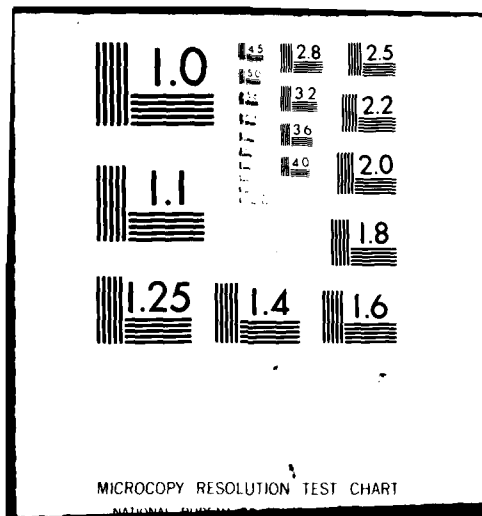
AD-A098 423

ROCKWELL INTERNATIONAL THOUSAND OAKS CA SCIENCE CENTER F/G 11/2  
RESEARCH OF MICROSTRUCTURALLY DEVELOPED TOUGHENING MECHANISMS I--ETC(U)  
MAR 81 F F LANGE N00014-77-C-0441  
SC5117.10TR NL

UNCLASSIFIED

1 of 1  
AD-A098 423

END  
DATE  
FILMED  
5-81  
DTIC



AD A098423

DTIC FILE COPY

LEVEL

(2)



Rockwell International  
Science Center

SC5117.10TR

*Oct 1980*

# TRANSFORMATION TOUGHENING

## PART 3: EXPERIMENTAL OBSERVATIONS IN THE $ZrO_2$ - $Y_2O_3$ SYSTEM

F.F. Lange

*MMR-81*

Structural Ceramics Group  
Rockwell International Science Center  
Thousand Oaks, California 91360

### ABSTRACT

*N00014-77-C-0441*

Materials in the  $ZrO_2$ - $Y_2O_3$  system ( $< 7.5$  m/o  $Y_2O_3$ ) were fabricated to investigate the conditions required to retain the metastable, tetragonal phase and to determine the contribution of the stress-induced martensitic reaction to fracture toughness. Retention of the tetragonal phase was optimized by minimizing porosity and maintaining the grain size below a critical value. The critical grain size increased from  $0.2 \mu m$  to  $1 \mu m$  for compositions ranging between 2 m/o  $Y_2O_3$  to 3 m/o  $Y_2O_3$ , respectively. These results are consistent with the theories developed regarding the thermodynamics of the martensitic reaction in a constrained state. In the tetragonal plus cubic phase field (compositions between 3.0 and 7.5 m/o  $Y_2O_3$ ), the critical stress intensity factor decreased from  $6.3 MPa \cdot m^{1/2}$  to  $3.0 MPa \cdot m^{1/2}$  as the volume fraction of the retained, tetragonal phase decreased to zero. Theoretical results, derived from the concept that the crack's stress field does work to unconstrain the transformation, are in good agreement with the experimental results.

DTIC  
ELECTE  
S MAY 4 1981 D

1 81 5 04 114

C2707A/jbs

This document has been reviewed  
for public release and is in  
distribution is unlimited.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(12) 21

## REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS  
BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

AD A098423

4. TITLE (and Subtitle)

5. TYPE OF REPORT & PERIOD COVERED  
Technical Report No. 10  
12/01/80 through 04/01/81Research of Microstructurally Developed Toughening Mechanisms in Ceramics. Part 3.  
Experimental Observations in

6. PERFORMING ORG. REPORT NUMBER

SC5117.1PTR

7. AUTHOR

ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> 3.1.1

8. CONTRACT OR GRANT NUMBER(s)

N00014-77-C-0441

F.F./Lange

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Rockwell International Science Center  
1049 Camino dos Rios  
Thousand Oaks, CA 9136010. PROGRAM ELEMENT, PROJECT, TASK  
AREA & WORK UNIT NUMBERS

032-574(471)

11. CONTROLLING OFFICE NAME AND ADDRESS

Director, Metallurgy Programs, Material Sciences  
Office of Naval Research, 800 N. Quincy Street  
Arlington, VA 22217

12. REPORT DATE

March 1981

13. NUMBER OF PAGES

19

14. MONITORING AGENCY NAME &amp; ADDRESS (if different from Controlling Office)

(9) Technical rpt. no. 10  
1 Dr. SP-1 Apr 81

15. SECURITY CLASS. (of this report)

Unclassified

15a. DECLASSIFICATION/DOWNGRADING  
SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Fracture toughness, martensitic transformations, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, phase transformation, strengthLess than or  
equal to

ABSTRACT (Continue on reverse side if necessary and identify by block number)

Materials in the ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> system (7.5 m/o Y<sub>2</sub>O<sub>3</sub>) were fabricated to investigate the conditions required to retain the metastable, tetragonal phase and to determine the contribution of the stress-induced martensitic reaction to fracture toughness. Retention of the tetragonal phase was optimized by minimizing porosity and maintaining the grain size below a critical value. The critical grain size increased from 0.2  $\mu$ m to 1  $\mu$ m for compositions ranging between 2 m/o Y<sub>2</sub>O<sub>3</sub> to 3 m/o Y<sub>2</sub>O<sub>3</sub>, respectively. These results are consistent with the theories developed regarding the thermodynamics of the

DD FORM 1473 EDITION OF 1 NOV 68 IS OBSOLETE

UNCLASSIFIED microimeters

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

389949

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

martensitic reaction in a constrained state. In the tetragonal plus cubic phase field (compositions between 3.0 and 7.5 m/o  $Y_2O_3$ ), the critical stress intensity factor decreased from  $6.3 \text{ MPa}\cdot\text{m}^{1/2}$  to  $3.0 \text{ MPa}\cdot\text{m}^{1/2}$  as the volume fraction of the retained, tetragonal phase decreased to zero. Theoretical results, derived from the concept that the crack's stress field does work to unconstrain the transformation, are in good agreement with the experimental results.

UNCLASSIFIED

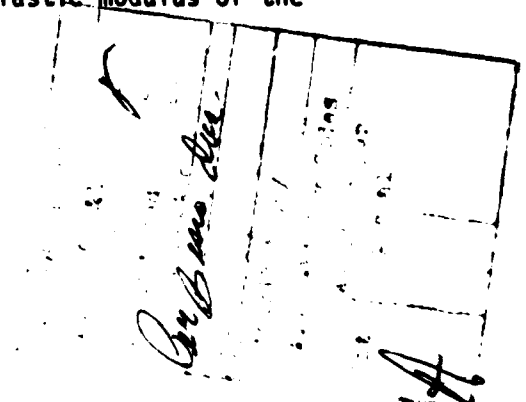
SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)



## Introduction

The first part<sup>1</sup> of this series presented a thermodynamic analysis to explain the size effect associated with a constrained phase transformation. It was shown that a critical inclusion (or grain) size exists, below which the constrained transformation is thermodynamically unfavorable. The size effect arises from surface phenomena associated with the transformation, viz. twinning and/or microcracking, which relieve constraint. These surface phenomena can be avoided when the material is fabricated with an inclusion size less than the critical size. It was further shown that the critical size could be increased by either increasing the elastic modulus of the constraining matrix or alloying to lower the chemical free energy change associated with the transformation. From a practical viewpoint, increasing the critical size can relax the constraints imposed on the fabricator who must contend with inclusion coarsening and grain growth during heat treatment and/or sintering.

In Part 2,<sup>2</sup> the contribution of the constrained inclusions to the fracture toughness was analyzed. It was shown that the energy absorbed in the fracture process was equivalent to the work performed by the loading system to stress-induce the transformation. The contribution of the stress-induced transformation was thus shown to be related to the chemical free energy change associated with the transformation, the volume of material that remains in the transformed state during crack extension and the elastic modulus of the composite.





The present part reports the experimental work with materials in the  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  system and is concerned with both retention of the high temperature tetragonal structure of  $\text{ZrO}_2$  and its effect on fracture toughness. Figure 1 illustrates<sup>3,4</sup> that  $\text{Y}_2\text{O}_3$  forms a solid solution with  $\text{ZrO}_2$  and lowers the tetragonal  $\rightarrow$  monoclinic transformation temperature from  $\sim 1200^\circ\text{C}$  to  $\sim 565^\circ\text{C}$  at a  $\text{Y}_2\text{O}_3$  content of  $\sim 3.5$  mole %. Thus, effects concerned with changing the chemical free energy could be studied with  $\text{Y}_2\text{O}_3$  additions up to  $\sim 3.5$  m/o. Figure 1 also shows a two phase, tetragonal + cubic, field exists between  $\sim 3.5$  m/o  $\text{Y}_2\text{O}_3$  and  $\sim 7$  m/o  $\text{Y}_2\text{O}_3$ , in which a two-phase material could be fabricated to determine the effect of the tetragonal phase content on fracture toughness. The  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  system appeared to be useful in obtaining data that may support some of the theoretical predictions made in Parts 1 and 2. In addition, Gupta et al,<sup>5</sup> have already demonstrated that single phase, tetragonal  $\text{ZrO}_2$  could be fabricated in this system. Experimental effort was thus concentrated in three areas: 1) effect of density on retention of the tetragonal phase, 2) the critical grain size required for phase retention, and 3) the fracture toughness as related to composition.

### 3. Experimental Procedures

Composite powders (0 - 7.5 m/o  $\text{Y}_2\text{O}_3$ ) were prepared by mixing in a mortar and pestal submicron size  $\text{ZrO}_2$  powder\* with the appropriate amount of yttrium nitrate in methanol, after determining the conversion factor for the

---

\*Zicar Corp., Florida, N.Y.

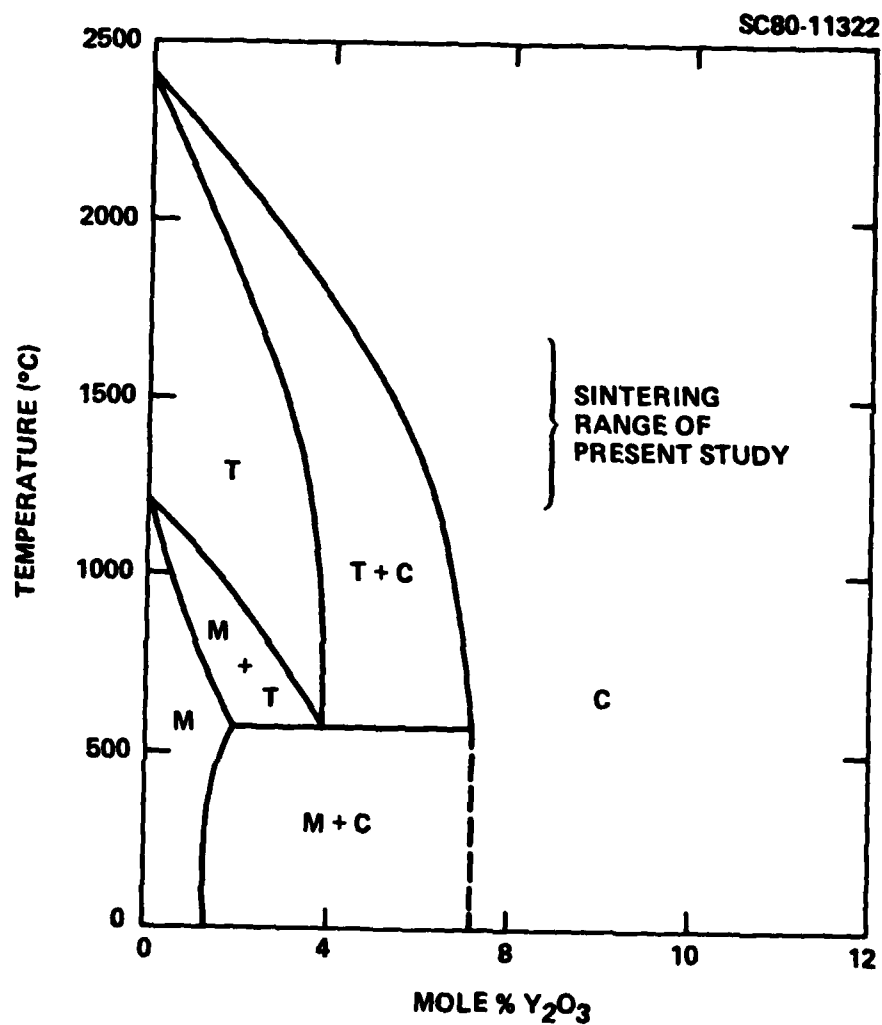


Fig. 1 The portion of the  $ZrO_2$ - $Y_2O_3$  system used in the present work.<sup>3,4</sup>





decomposition of yttrium nitrate to  $Y_2O_3$ . Prior to cold pressing and sintering, the composite powders were calcined for 4 hrs at  $400^\circ C$ . Sintering experiments were performed in an air environment at temperatures between  $900^\circ$  and  $1650^\circ C$ . After sintering, densities\* were obtained by either dimensional/weight measurements or a water displacement technique. X-ray diffraction was used for phase identification. Monoclinic and tetragonal phase contents were determined from their relative intensity ratios of their respective (111) and (111) diffraction peaks by using a planometer. The presence of the cubic phase was determined by both the (311) and the (400) diffraction peaks which would split the respective diffraction peaks of the tetragonal phase.

For selected materials the critical stress intensity factor,  $K_{IC}$ , was determined at room temperatures by using the indentation technique developed by Evans and Charles.<sup>6</sup> Prior to using this technique, the surface of each specimen was finely polished and x-rayed to ensure that the surface was not noticeably altered by the preparation procedure. It should be noted that rough grinding will induce the tetragonal  $\rightarrow$  monoclinic transformation at the surface, and the damaged layer can be removed (within current detectability limits of  $\sim 0.5 \mu m$ )<sup>7</sup> by polishing. The intercept method was used to determine grain size on SEM micrographs of fracture surfaces.

---

\*The theoretical density of  $ZrO_2/Y_2O_3$  materials were calculated from Scott's<sup>4</sup> lattice parameter data.



### 3. Results and Discussion

#### 3.1 General Fabrication Observations

Approximately 80% of the total shrinkage occurred rapidly ( $< 2$  hrs) between  $1150^{\circ}$  and  $1250^{\circ}\text{C}$ ; further shrinkage required temperatures  $> 1350^{\circ}\text{C}$ . Densities of 82% to 87% theoretical could be achieved at  $1200^{\circ}\text{C}/24$  hrs. For compositions containing  $< 6$  m/o  $\text{Y}_2\text{O}_3$ , densities of 88% to 93% theoretical could be achieved by sintering 24 hrs at  $1200^{\circ}\text{C}$  followed by 2 hrs at  $1400^{\circ}\text{C}$ . Compositions containing  $> 6$  m/o  $\text{Y}_2\text{O}_3$  required an additional 2 hrs at  $1550^{\circ}\text{C}$ .

#### 3.2 Retention of Tetragonal $\text{ZrO}_2$ : Effect of Density

Composite powders containing 2.5 m/o  $\text{Y}_2\text{O}_3$  were uniaxial cold pressed at different stresses to achieve different grain densities and then were sintered together for 2 hrs at  $1500^{\circ}\text{C}$ . Figure 2 plots the results of this experiment in terms of the % retained tetragonal phase vs the % of theoretical density achieved during sintering. It can be concluded that the retention of the high temperature tetragonal phase at room temperature depends on the density achieved during fabrication. This conclusion shows that phase retention is directly related to the constraint imposed by neighboring grains on one another. Porosity lowers the elastic modulus and introduces free surface. The effect of both of these factors would reduce the strain energy associated with the transformation allowing larger grains and/or grains bounded by more free surface than neighboring grains to undergo the transformation during cooling.<sup>1</sup>

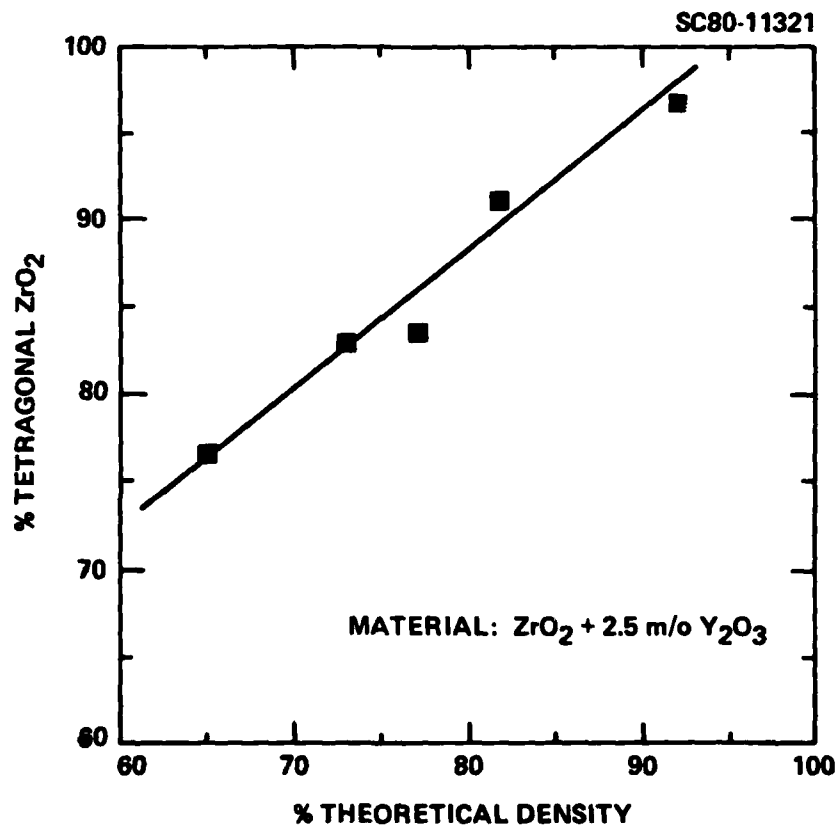


Fig. 2 The effect of density on retention of tetragonal ZrO<sub>2</sub> + 2.5 m/o Y<sub>2</sub>O<sub>3</sub>.



### 3.3 Retention of Tetragonal $ZrO_2$ : Critical Grain Size

Composite powders containing 0, 1.5, 2.0, 2.5, 3.0 and 3.5 m/o  $Y_2O_3$  were cold pressed and sintered for 2 hrs at temperatures ranging from 1200° to 1600°C. Detailed grain size measurements were made on the 2.0 m/o  $Y_2O_3$  composition as a function of temperature; these results are shown in Fig. 3. Measurements on other selected compositions were in agreement with these data. The phase content of each specimen was compared to the grain size measurement in order to determine the critical grain size required to retain > 90% of the tetragonal phase. Since densities between 80% and 90% of theoretical could only be achieved with the sintering conditions stated, monoclinic contents < 10% were neglected. (If full density could be achieved, the critical grainsize would be expected<sup>1</sup> to be somewhat smaller than those reported in Fig. 4.)

As shown in Fig. 4, a high tetragonal content could not be achieved for the composition containing 1.5 m/o  $Y_2O_3$ , i.e., grain growth during sintering precluded an average grain size < 0.2  $\mu m$ . The pure  $ZrO_2$  was completely monoclinic under all conditions. More important, Fig. 4 shows that the average critical grain size significantly increases between 2 and 3 m/o  $Y_2O_3$ . The composition containing 3.5 m/o  $Y_2O_3$  contained a detectable amount of cubic phase, indicating that it lies in the tetragonal + cubic phase field at temperatures > 1200°C (see Fig. 1).

The increase in the critical grain size with increasing  $Y_2O_3$  content is consistent with the theoretical prediction that the critical grain size would increase as the magnitude of the change in chemical free energy decreases (see Part 1).

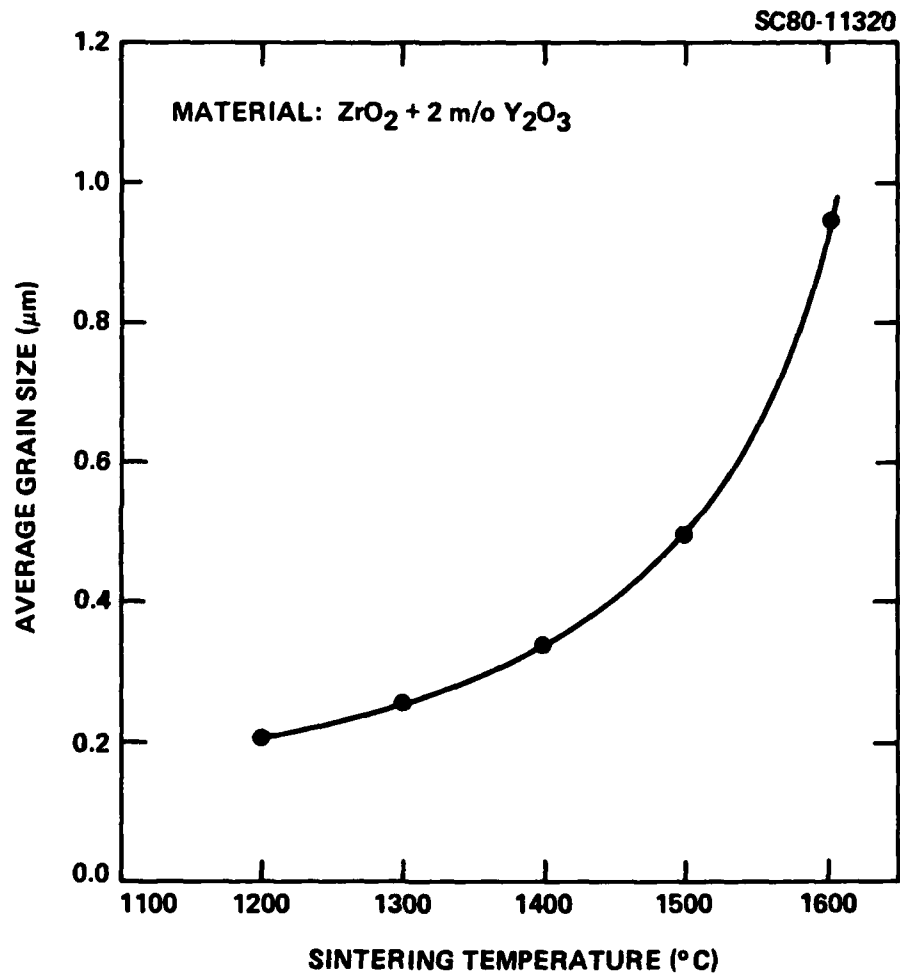


Fig. 3 Average grain size vs sintering temperature determined for the  $\text{ZrO}_2$  material containing 2 m/o  $\text{Y}_2\text{O}_3$ .

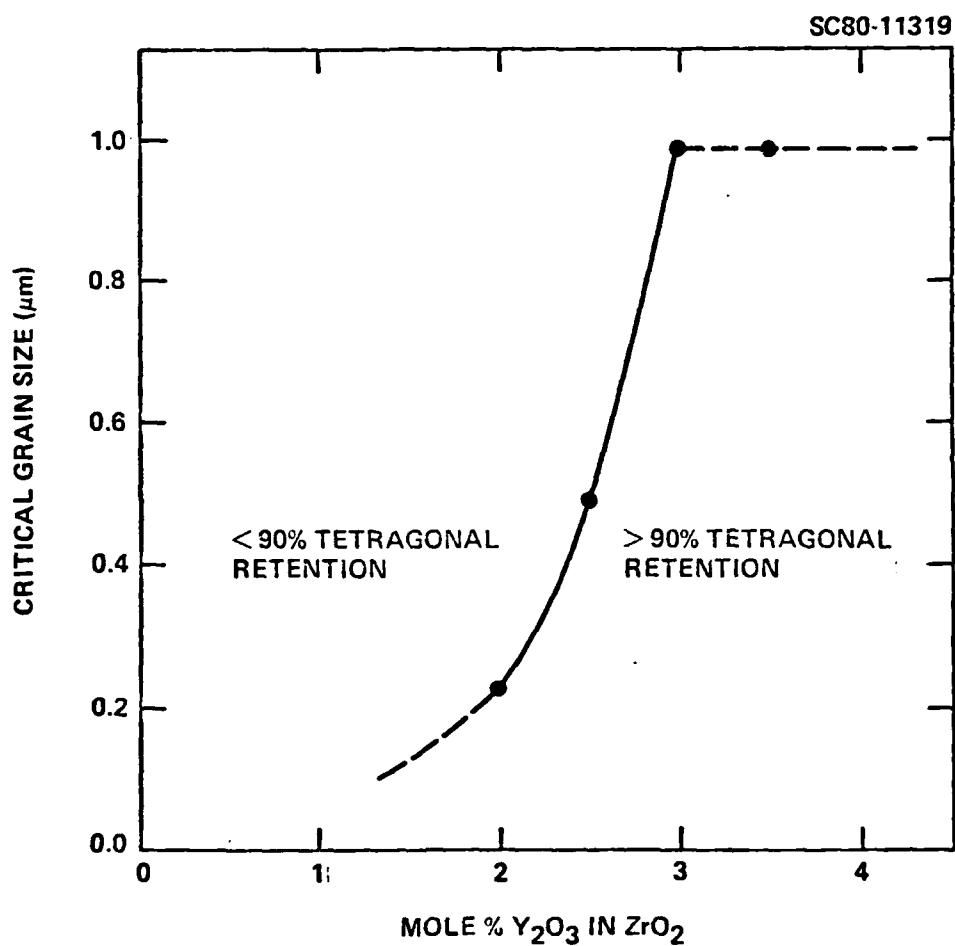


Fig. 4 Critical grain size vs  $\text{Y}_2\text{O}_3$  content in tetragonal  $\text{ZrO}_2$ .



SC5117.10TR

### 3.4 Fracture Toughness

The object of this task was to measure fracture toughness as a function of the retained tetragonal phase. Composite powders containing 1.5 to 7.5 m/o  $Y_2O_3$  in increments of 0.5 m/o  $Y_2O_3$  were prepared. According to Fig. 1, compositions with  $> 3$  m/o  $Y_2O_3$  should contain increasing contents of the cubic phase. Sintering schedules were optimized (see Section 3.1) to produce materials with a density in the range of 88% to 93% of theoretical. Phase identification results were consistent with the concepts required for retention of the tetragonal phase and the phase diagram for this system (Fig. 1). A two phase, tetragonal + cubic, material was produced between 3 m/o  $Y_2O_3$  and 7 m/o  $Y_2O_3$ ; the volume fraction of the tetragonal phase decreased from one at 3.0 m/o  $Y_2O_3$  to zero at 7.0 m/o  $Y_2O_3$ . Only the 1.5 m/o  $Y_2O_3$  composition contained an appreciable amount ( $> 10\%$ ) of the monoclinic phase, because the average grain size was in excess of the critical value. The monoclinic phase was not detected in compositions containing  $> 3$  m/o  $Y_2O_3$ .

Results of the stress intensity factor measurements are shown in Fig. 5 as a function of the  $Y_2O_3$  content and the volume content of the tetragonal phase. Three indentations were used to determine  $K_C$  for each composition; data scatter illustrates high and low values. This figure shows that  $K_C$  drops from  $6.3 \text{ MPa} \cdot \text{m}^{1/2}$  to  $3.0 \text{ MPa} \cdot \text{m}^{1/2}$  as the volume fraction of the tetragonal phase decreases to zero. The 1.5 m/o  $Y_2O_3$  composition had a relatively low  $K_C$  due, apparently, to the large amount of monoclinic phase.

The solid line in Fig. 5 was obtained from the calculated effect of the tetragonal volume fraction on  $K_C$  by using<sup>2</sup>



SC80-11318

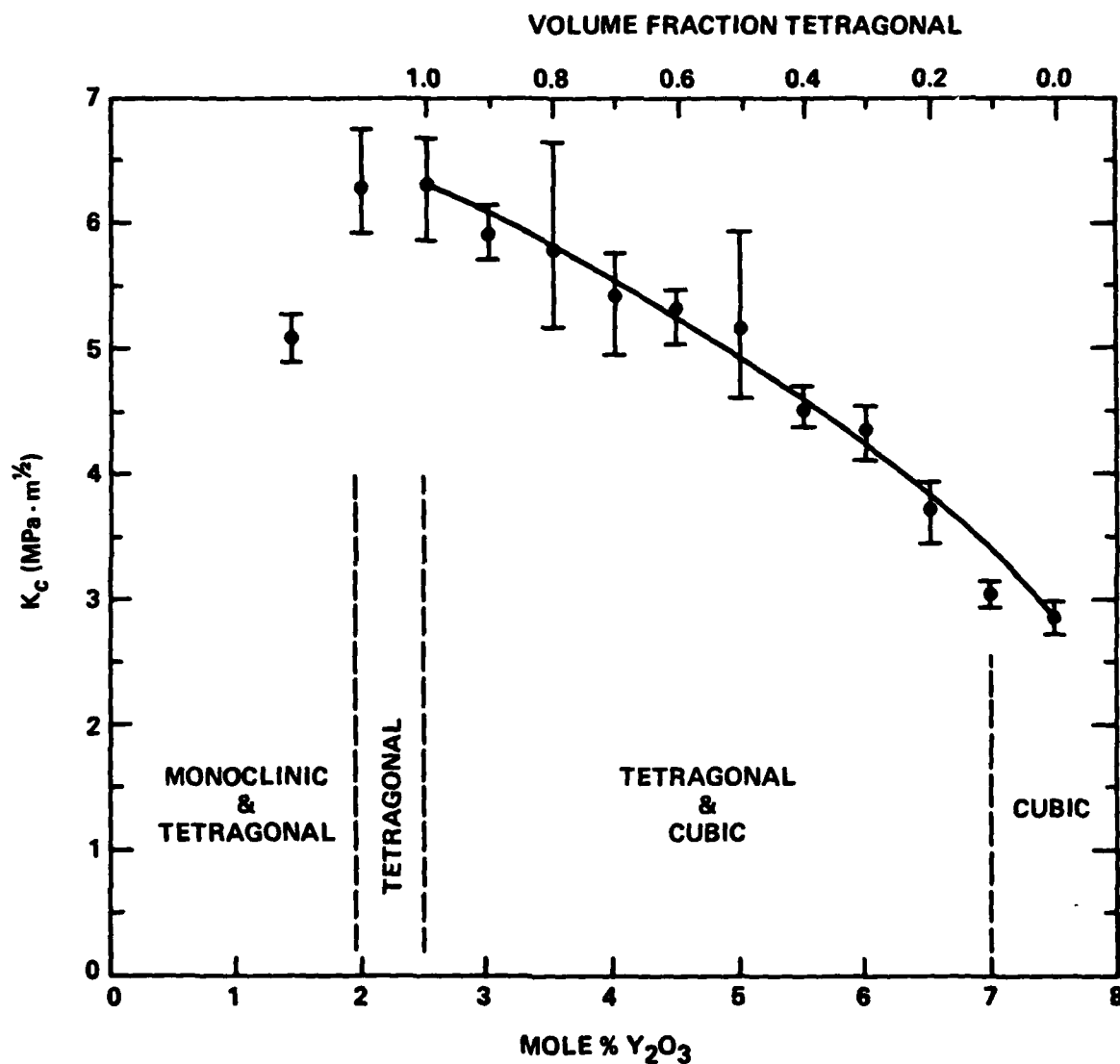


Fig. 5 Fracture toughness ( $K_c$ ) vs mole % of  $Y_2O_3$  in  $ZrO_2$ .





SC5117.10TR

$$K_c = \left[ K_0^2 + \frac{2(|\Delta G^C| - \Delta U_{sef}) E_c V_f R}{(1 - \nu_c^2)} \right]^{1/2}, \quad (1)$$

where:

- $K_0$  = the fracture toughness of the cubic phase ( $3.0 \text{ MPa}\cdot\text{m}^{1/2}$ ),
- $|\Delta G^C|$  = the magnitude of the chemical free energy change associated with the transformation,
- $\Delta U_{sef}$  = the residual strain energy associated with the transformed grains near the fracture surface
- $E_c, \nu_c$  = the elastic modulus and Poisson's ratio of the composite,
- $R$  = the depth of the transformation zone from the fracture surface, and
- $V_f$  = the volume fraction of the tetragonal phase.

Equation (1) can be rewritten as

$$K_c^2 - K_0^2 = C V_f, \quad (2)$$

where  $C$  can be evaluated where  $V_f = 1.0$  to predict the effect of volume fraction. As shown, the predicted effect of the tetragonal volume fraction on  $K_c$  is in perfect agreement with the experimental values.

By assuming that the depth of the transformation zone is approximately equivalent to the grain size,<sup>2</sup> one can use Eq. (1), the experimental values of  $K_c$  and  $K_0$ , and the expected elastic properties of the material to determine the fac-



SC5117.10TR

tor ( $|\Delta G^c| - \Delta U_{sef}$ ). This factor is the work per unit volume loss during the stress induced transformation.<sup>2</sup> Using the values  $E_c = 165 \text{ GPa}^*$ ,  $\nu_c = 0.25$  and  $R = 0.5 \text{ } \mu\text{m}$ , the work done per unit volume of transformed material was calculated as  $176 \text{ MJ/m}^3$ .

### 3.5 Fractography

Figure 6 illustrates the typical fracture surface topography of four compositions (2 m/o  $\text{Y}_2\text{O}_3$ , major: monoclinic, minor: tetragonal; 3.5 m/o  $\text{Y}_2\text{O}_3$ , major: tetragonal, trace: cubic; 7.5 m/o  $\text{Y}_2\text{O}_3$ , major: cubic; 5 m/o  $\text{Y}_2\text{O}_3$ , major: cubic, minor: tetragonal; all  $\sim 85\%$  dense), sintered at  $1600^\circ\text{C}$  for 2 hrs. Intergranular fracture (Fig. 6a) was typical of the high monoclinic materials, suggesting that the crack path followed the intergranular microcracks produced during fabrication as a result of the phase transformation. Such materials were quite friable. Irregular, transgranular fracture was typical of tetragonal materials (Fig. 6b). The irregular fracture topography of individual grains may be a result of the cracks interacting with the complex internal structure of the twinned monoclinic grains. Fig. 6b also indicates that intergranular microcracks were not produced ahead of the crack front, because of the stress-induced transformation, i.e., if microcracks were present, the fracture surface would resemble that shown in Fig. 6a. A smooth transgranular fracture surface was typical for the cubic materials (Fig. 6c). The porosity ( $\sim 15\%$ ) associated with these materials is easily recognized in the cubic material because of the near planar topography

\*The elastic modulus of dense  $\text{ZrO}_2(t)$  is  $207 \text{ GPa}$ ,<sup>8</sup> the value of  $165 \text{ GPa}$  was calculated for a material with  $10\%$  porosity.

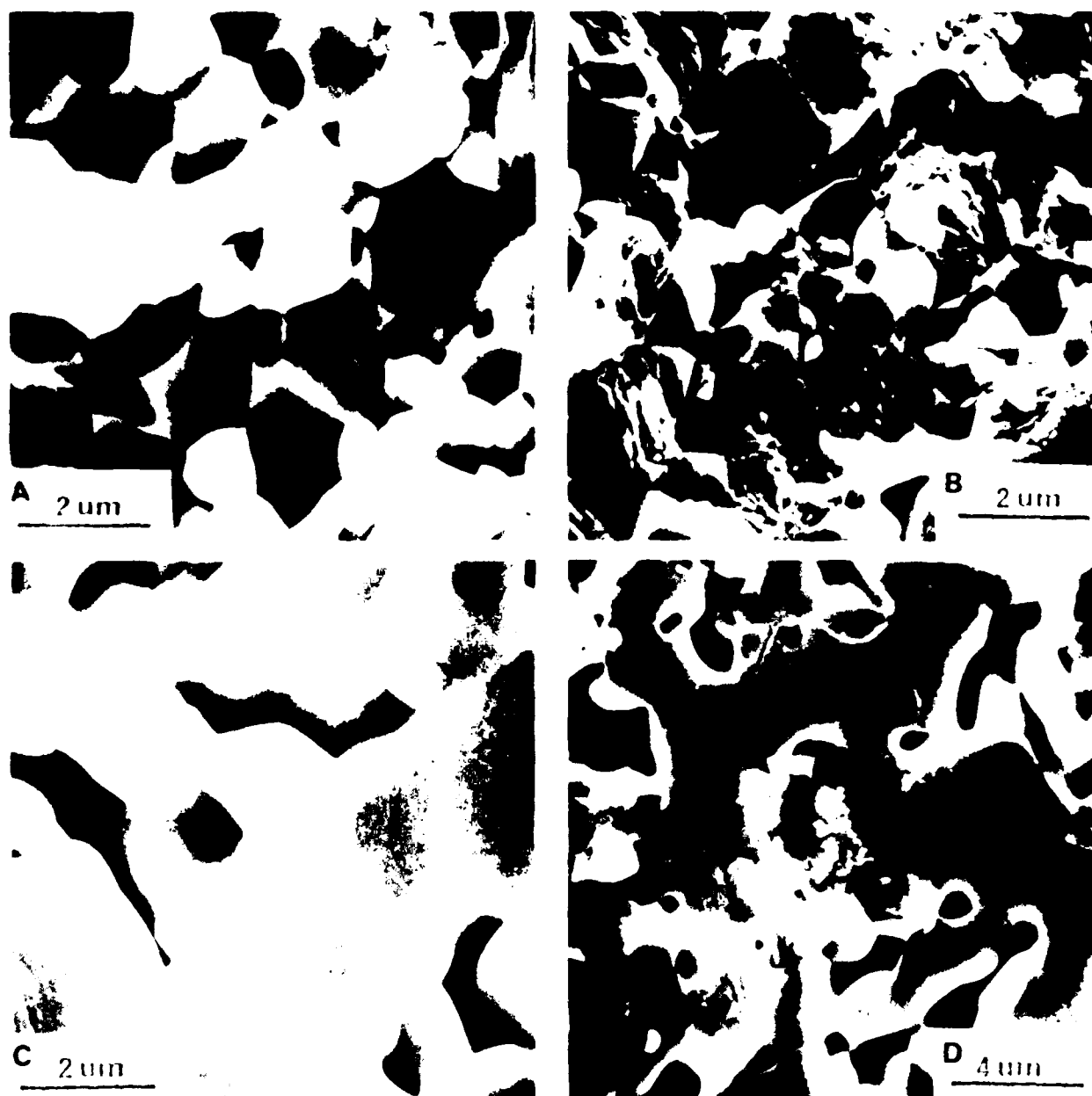


Fig. 6 Fracture surfaces of a) monoclinic  $\text{ZrO}_2$  + 2 m/o  $\text{Y}_2\text{O}_3$  composition, b) tetragonal  $\text{ZrO}_2$  + 3.5 m/o  $\text{Y}_2\text{O}_3$  composition, c) cubic  $\text{ZrO}_2$  + 7.5 m/o  $\text{Y}_2\text{O}_3$ , and d) mixed tetragonal + cubic  $\text{ZrO}_2$  + 5 m/o  $\text{Y}_2\text{O}_3$ . All sintered at  $1600^\circ\text{C}/2$  hrs.



SC5117.10TR

of the fracture surface. Since both the tetragonal and cubic phases produce different fracture topographies, it was relatively easy to recognize tetragonal grains surrounded by cubic grains for two phase compositions such as the 5 m/o  $Y_2O_3$  composition shown in Fig. 6d. This observation suggests that the two phases in such compositions ( $3 \text{ m/o} < Y_2O_3 < 6.5 \text{ m/o}$ ) are present as separate grains, instead of tetragonal precipitates within a cubic matrix as produced by fabricating in the cubic phase field and quenching into the tetragonal + cubic phase field.<sup>9</sup>

#### 4. Conclusions

Retention of the tetragonal phase was found to depend on both density and grain size. The dependence on density is consistent with the need for self-constraint and with the concepts developed regarding the thermodynamics of the martensitic reaction in an elastically constrained matrix. The effect of  $Y_2O_3$  on the critical grain size is consistent with the theory relating the chemical free energy change to the size effect produced by surface phenomena (e.g., twinning and microcracking) that can accompany the transformation.

The contribution of the stress-induced transformation to the fracture toughness is significant and is directly related to the volume fraction of the retained tetragonal phase. Theory developed to explain this contribution is in good agreement with experimental data validating the concept that the transformation's contribution lies with the work done to unconstrain the martensitic reaction. Fractography indirectly supports this concept.



### Acknowledgement

The author wishes to thank M.G. Metcalf for technical services. This work was supported by the Office of Naval Research, Contract N00014-77-C-0441.

### References

1. F.F. Lange, "Part 1: Size Effects Associated with Constrained Phase Transformations."
2. F.F. Lange, "Part 2: Contribution to Fracture Toughness."
3. K.K. Srirastaka, R.N. Patil, C.B. Chandry, K.V.G.K. Gokhale and E.C. Subbaro, "Revised Phase Diagram of the System  $ZrO_2-YO_{1.5}$ ," Trans. Brit. Ceram. Soc. 73, 85 (1974).
4. H.G. Scott, "Phase Relations in the Zirconia-Yttria System," J. Mat. Sci, 10, 1527 (1975).
5. T.K. Gupta, F.F. Lange and J.H. Bechtold, "Effect of Stress-Induced Phase Transformation on the Properties of Polycrystalline  $ZrO_2$ ," J. Mat. Sci 13, 1464 (1978).
6. A.G. Evans and E.A. Charles, "Fracture Toughness Determination by Indentation," J. Am. Ceram. Soc. 59 (7-8), 371 (1976).



7. F.F. Lange and A.G. Evans, "Erosive Damage Depth in Ceramics: A Study on Metastable, Tetragonal Zirconia," J. Am. Ceram. Soc. 62[1], 62 (1979).
8. F.F. Lange, "Part 4: Fabrication, Phase Retention and Fracture Toughness Observations in the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  System."
9. R.G. Garvie and R.T. Pascoe, Processing in Crystalline Ceramics ed. by H. Palmour III, R.F. Davis and T.M. Hare, p. 263, Plenum Press (1978).